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OCCURRENCE OF GAS HYDRATES IN THE COMETARY NUCLEI

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SUMMARY

Quantitative considerations show that OH productions, provided by observations on cometary heads, are compatible with the H_2O sublimation rates of water ice or hydrate ices present within the nucleus.

As the presence of H_2O molecule within the nucleus is thus confirmed by circumstantial considerations, thermodynamic evidence leaves little alternate possibility to the presence of clathrate CH_4 hydrate (if there is any CH_4) of ionic NH_3 hydrate (if there is any NH_3) etc...

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Some time ago Delsemme and Swings (1952) pointed out the great difficulty encountered in the Whipple model of cometary nucleus (1950), interpreted as a conglomerate of ice. It seems that at present it has become possible to discuss the eventual presence of gas hydrates by means of more quantitative considerations than in the past. Before going ahead with this discussion, it is appropriate to recall, first of all, the nature of the difficulty to be resolved.

It is well known that the sublimation rates in the vacuum of H_2O, CH_4 and NH_3 ices have extraordinarily different orders of magnitude for a given temperature, and this difference subsists for a very broad temperature range. For example, at about $100°$ K, the sublimation rate of CH_4 is of the order of 10^7 times that of NH_3 and of 10^{14} times that of H_2O. It is true, however, that one cannot observe mother-molecules, but, if they really exist, the results of their photodissociation ought to reflect these considerable differences, which is not the case.

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* Occurence des hydrates de gaz dans les noyaux cométaires.

This difficulty can be emphasized in another manner: the sublimation rate of CH_4 at 90° K is the same as that of NH_3 at 200° K and as the rate of evaporation of H_2O at 320° K. If the surface temperature of the nucleus followed approximately the well known relation in $r^{-\frac{1}{2}}$ (see Note 1), the sublimation rate of CH_4 at 19 a.u. from the Sun would be the same as that of NH_3 at 3.8 a.u. and that of the H_2O at 1.5 a.u. from the Sun. This too does not seem to be reconcilable with the distances of respective appearances of molecular bands in the spectra.

In order to forego this difficulty, it is simpler to assume that the molecular fragments, spectrally observed in the head, do not originate from as evident molecules, as those of which one has tendency to think in the first place, as for example CH_4, NH_3 and H_2O, but from a multitude of different chemical specie, namely those that have the property of narrowing considerably the orders of magnitude of all the sublimation rates. That is why Delsemme and Swings proposed in 1952 to consider most of volatile molecules as being able to be confined in hydrates. If, indeed, there were water ice in presence of CH_4, NH_3, CO_2, these molecules forcefully ought to have reacted among themselves to provide hydrates (ionic for HH_3; of the clathrate type for the other molecules),and all these hydrates would have· the remarkable properties of feeble water vapor tensions and of same order of magnitude.

Miller (1961) was the one who contributed most since 1952 to the understanding of the role of gas hydrates in the solar system. To do this, he studied their dissociation pressures from 0° to -12° C in laboratory conditions, which provided him with a very solid experimental basis for an extrapolation toward lower temperatures. His results allow the conclusion as that of Delsemme and Swings extrapolation, based upon the only data available in 1952, that is to say, the dissociation pressures established above the zero degree C for the system water — gas hydrate, led them to values ten times too low at -20° C, hundred times too low at -50° C and thousand times at -80° C. the difference increasing further toward low temperatures. The essential of their explanation remains, however, entirely valid, the methane vapor tensions diminishing nontheless by a factor of 10^{-3} to 10^{-6} (instead of 10^{-4} to 10^{-6}) when it is confined in a hydrate.

Another important contribution by Miller concerning the comets resides in his remark, that mixed hydrates will be forming eventually in place of a mixture of pure hydrates, for the latter are not stable in the presence of one another. (Refer to Note 2). Finally, Miller insisted with good reason on the argument, implied earlier, that hydrates will form necessarily because thermodynamics are favorable and rates of formation are sufficiently rapid.

This last assertion by Miller is, however, valid only in the hypothesis, whereby the presence of the H_2O molecule in the nucleus is not subject to doubt. Whipple had already suggested in 1950, that certain radicals could permanently exist in cometary nuclei at very low temperatures. Developing this idea, Haser (1955) proposed to consider that the radical OH itself could be substituted to H_2O in the midst of the cometary nucleus as the source of OH observed in the coma. The argument is that the spectrum of OH is observed at a too great distance from the Sun for its mother-molecule to be H_2O, water's vapor tension being too weak. Though this idea was never verified numerically, it was revived several times in literature, namely by Swings and Haser (1955) and Swings (1956). It desserves a quantitative examination, for it could become a crucial argument for the distinction between two possible origin of comets, the preservation of the radical OH being able to point to a very low-temperature origin, whereas its absence would not permit to reject a less cold origin.

A quantitative discussion is beset with several difficulties, of which the principal is relative to cometary nucleus' dimensions, as its radius plays a critical role in the calculations.

The current literature (See Note 3) leads us to accept here a 10 km radius as the most probable value for a comet of the Halley type. According to the Vorontsov-Velyaminov results (1960), recomputed on the basis of such a radius, the density of CN near the surface of the nucleus is in this case $8 \cdot 10^8$ and that of C_2 $4 \cdot 10^8$ molecules cm^{-3}.

Wurm (1963) has calculated $3 \cdot 10^9$ molecule cm^{-3} for both, C_2 and CN. Results obtained with weaker comets are not contradictory (see Note 4).

Combined at speeds of 0.5 — 1 km/sec established by Bobrovnikoff (1931), these values point to C_2 or CN productions of the order of 10^{14} molecule $cm^{-2} sec^{-1}$.

10^{14} molecule cm^{-2} sec^{-1}. If we take into account that the force of the oscillator of OH is thirty times weaker than that of CN or C_2, for the transitions observed (see Note 5), the ratio of the observed intensities lead to productions of OH comprised between 10^{14} and 10^{15} molecule cm^{-2} sec^{-1}.

On the other hand, Wurm (1963) computed the rate of the observed CO^+ production in the tail and found 10^{28} molecule cm^{-2} sec^{-1}. If CO^+ should originate from a mother-molecule of the nucleus, in vaporized state, this value would correspond to a minimum production of 10^{15} mol cm^{-2} sec^{-1} at the surface of a nucleus of 10 km radius. Grudzinska (1960) cross-checked this observation, finding that CO^+ is thirty times more abundant than CN per unit of volume. One can not thus reasonably admit 10^{15} mol cm^{-2} sec^{-1} as the mean probable value of OH production.

Elsewhere, the rate of H_2O evaporation can be computed and it is practically the same, starting from water or gas hydrate ices (see Note 6). Applying the theory of cometary nucleus' vaporization, as established by Delsemme (1965), we find the results of Table 1, which are compared with the results of observations mentioned above.

TABLE 1

Distance in astronom. u.	Production of H_2O mol cm^{-2} sec^{-1}	Production of OH cm^{-2} sec^{-1} near 1 a.u.
3.7	$3.9 \cdot 10^{16}$	-
2.2	$1.9 \cdot 10^{17}$	-
1.1	$9.6 \cdot 10^{17}$	10^{15}
0.6	$3.7 \cdot 10^{18}$	-

This Table clearly shows that there is no incompatibility of any sort between the productions of water vapor of a cometary nucleus and the results of observations relative to the production of radicals OH. , The orders of magnitude are verified and the rates observed, provided they are truly significative, correspond to a dissociation of 10^{-3} molecules

of water computed for 1.1 a.u., which does not appear to be unreasonable. Finally, since the production of H_2O is five times lower at a distance of 2.2 a.u. and since the intensity of the solar ultraviolet is there also 4 times weaker than at about 1.1 a.u., their production at about 2.2 a.u. must be of the order of 20 times lower than at 1.1 a.u., that is, of the photochemical dissociation of H_2O is indeed the source of radicals OH, and it becomes thus possible to explain the reason why the OH bands appear only between 1.5 and 2.0 a.u.

Therefore, the preceding evaluation shows that since the water vapor production does have a satisfactory order of magnitude, the Delsemme and Swings proposal of 1952 now rests upon a more solid quantitative argument What is too weak is not really the water vapor pressure, but the pressures of CH_4 and NH_3 vapors which are much too great to be compatible with the observations; to explain the latter it is necessary that CH_4 and NH_3 be fixed in steadier molecules, than in molecules of hydrates. At any rate, the presence of water implies necessarily the existence of these hydrates.

Elsewhere, and since the presence of water vapor seems to explain quantitatively the observations of the radical OH, there is no point to invoke the hypothesis that OH itself might exist in condensed state in the cometary nucleus, hypothesis, which incidently, does not lend itself to verification and is "ad hoc", so long as one is not aware of the latent heat, and thus of the evaporation rates of the condensed radical OH.

The result of the calculation must thus be retained as the proof of the existence of ices or snows of water or of hydrates, vaporizing the water vapor on nucleus' surface in sufficient quantity to justify the observed productions of OH. Observations of radicals CH and NH allow in their turn to conclude of the presence of hydrates that stabilize their mother-molecules CH_4 and NH_3.

**** T H E   E N D ****

ADDENDUM. - [Following are the various additional comments in the form of five notes, referred to in the preceding text.].

N O T E S

1. — In fact, since, as was shown elsewhere by the present author
   (Delsemme,A. H. - 1965), the temperature varies at a slower pace
   with the law in $r^{-\frac{1}{2}}$, the situation is still more unfavorable.

2. - The existence of mixed hydrates apparently renders the problem of
   dissociation tensions still more complex, for since they combine
   in any proportions, in order to represent their behavior the entire
   network of curves depending on their relative tenor in CH_4, NH_3 etc.
   will now be required instead of the unique curve of the dissociation
   pressure for a pure hydrate as a function of temperature.

   In practice, however, it has not been proved as yet that
   mixed hydrates play an important role in the cometary nucleus (see
   about this subject, Delsemme 1965).

3. - It is appropriate to recall some characteristic results allowing
   to have a glimpse of our knowledge on the subject. Wurm (1943)
   and Vorontsov-Velyaminov (1946) have derived photometrically that
   the Halley Comet has a radius of 20 km. Liller (1960) has calcula-
   ted the dust losses by perihelion passages on two comets of the
   Halley comet class. Whipple (1963) has derived therefrom the mini-
   mum masses corresponding to a radius from 3 to 14 km. It is however
   necessary to recall two evaluations by Baldet for two smaller comets
   relative to two cometary passages close to one another (0.039 and
   0.056 a.u.), where basing himself upon the absolute magnitude of
   the nucleus seen at great magnification by means of the Meudon
   telescope, he concluded of radii less than 200 meters in both cases.
   Finally, the compilation of some thirty possible values of radii
   of cometary nuclei, presented in the paper by Miss Roemer on the
   occasion of the current colloquium, is particularly significative.

4. - In particular, when Houziaux (1960) found 70 molecules of C_2 per
   cm^3 at 50 000 km from the nucleus, the law in r^{-2} would give
   $2 \cdot 10^9$ for a radius of 10 km. Even if the attenuation does not obey
   the law in r^{-2} , the observations are in no way incompatible with

densities of same order around a nucleus, of which the radius may be less than 1 km.

5.- For the transitions $(A^2\Sigma - X^2\Pi)$ of OH, the oscillator force is of $8 . 10^{-4}$ whereas for the transition $(A^3\Pi - X^3\Pi)$ of C_2, it is equal to $2.4 . 10^{-2}$.

It should be noted here that the rate of evaporation of H_2O depends little on its origin, whether this be water ice or that of gas hydrate. Indeed, if the existence of hydrates replaces the vapor tensions of such gases as CH_4 by dissociation tensions of the correspondent hydrate which are considerably lower (factor of 10^{-6} at $100°K$ for CH_4, for example), this existence of hydrates, on the contrary, does not appreciably modify the water vapor tension or that of water ice. Indeed, the products of hydrate dissociation are methane (gas) and a solid crystalline network of ice (water) with empty gaps. This ice (or snow) of water evidently has a crystallization system slightly different, which imparts to it a different water vapor pressure, however, hardly different from the ordinary ice.

:::: E N D   O F   N O T E S ::::

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